# IMPROVED REACTIVITY ESTIMATES FOR VOLATILE ORGANIC COMPOUNDS USED IN ARCHITECTURAL COATINGS

BY

WILLIAM P. L. CARTER

COLLEGE OF ENGINEERING CENTER FOR
ENVIRONMENTAL RESEARCH AND TECHNOLOGY
UNIVERSITY OF CALIFORNIA, RIVERSIDE

August 15, 2001

## OUTLINE

**UNCERTAINTIES IN REACTIVITY SCALES**

**REACTIVITY RESEARCH NEEDS FOR ARCHITECTURAL COATINGS**

**COMPONENTS OF CE-CERT COATINGS PROJECT AS CURRENTLY FUNDED**

**COMPONENTS OF PROPOSED EXTENSION FOR COATINGS REACTIVITY PROJECT**

**ENVIRONMENTAL CHAMBER STUDIES**

**PRIORITIES FOR COMPOUNDS TO BE STUDIED**

**DIRECT REACTIVITY STUDIES**

# UNCERTAINTIES IN REACTIVITY SCALES

## UNCERTAINTY IN THE GENERAL APPLICABILITY OF ANY SINGLE SCALE

- NO SCALE CAN REPRESENT ALL ENVIRONMENTS.
- NOT ALL EXPERTS AGREE THAT THE MIR SCALE IS THE MOST APPROPRIATE FOR REGULATIONS.
- CALIFORNIA HAS ADOPTED THE MIR SCALE. THE EPA WANTS MORE RESEARCH BEFORE ADOPTING A SCALE FOR REGULATIONS.

## CHEMICAL MECHANISM UNCERTAINTY

- GENERAL MECHANISM UNCERTAINTIES CAUSE UNCERTAINTY FOR EVEN WELL-STUDIED VOCs.
- UNCERTAINTIES ARE MUCH GREATER FOR VOCs WITH NO DATA TO VERIFY THEIR MECHANISMS.

## COMPOSITION UNCERTAINTY

- APPLICABLE TO COMPLEX MIXTURES SUCH AS VEHICLE EXHAUSTS AND PETROLEUM DISTILLATES

# REACTIVITY RESEARCH NEEDS FOR VOCs FOR ARCHITECTURAL COATINGS

REACTIVITY DATA ARE ALREADY AVAILABLE FOR MANY TYPES OF VOCs USED IN COATINGS

- DATA AVAILABLE FOR REPRESENTATIVE ALKANES, AROMATICS, ALCOHOLS, GLYCOLS, ESTERS, ESTERS AND A FEW OTHERS.
- BUT NOT ALL ASPECTS OF MECHANISMS ARE ADEQUATELY EVALUATED.

REACTIVITY ESTIMATES ARE UNCERTAIN FOR SOME IMPORTANT TYPES OF COATINGS VOCs

- NO DATA FOR LOW VOLATILITY COMPOUNDS SUCH AS TEXANOL
- PETROLEUM DISTILLATES HAVE LARGE COMPOSITIONAL UNCERTAINTY
- DATA NEEDED TO EVALUATE REACTIVITIES PETROLEUM DISTILLATES WITH AROMATICS
- NO DATA TO EVALUATE $O_3$ IMPACT PREDICTIONS FOR ETHYLENE GLYCOL

NEED TO DEVELOP LOWER COST REACTIVITY SCREENING AND ENFORCEMENT METHODS

UNCERTAIN HOW MUCH DEPOSITION ON SURFACES AND OTHER NON-ATMOSPHERIC LOSS PROCESSES ARE AFFECTING ATMOSPHERIC AVAILABILITY

# COMPONENTS OF CURRENT CE-CERT COATINGS PROJECT FOR THE CARB

CONDUCT EMISSIONS, REACTIVITY AND UNCERTAINTY SURVEY OF COATINGS VOCs

- PRELIMINARY EVALUATION COMPLETED TO PRIORITIZE RESEARCH

CONDUCT ENVIRONMENTAL CHAMBER STUDIES OF A SELECTED COATINGS VOC

- THE "NEXT GENERATION" CHAMBER BEING DEVELOPED FOR THE EPA WILL BE USED
- EXISTING EPA FUNDING WILL COVER COST OF INITIAL CHARACTERIZATION RUNS
- SUFFICIENT FUNDING FOR 6 EXPERIMENTS WITH TEXANOL

DEVELOP A DIRECT REACTIVITY SCREENING FOR APPLICATION TO COATINGS CONSTITUENTS

- ADAPT CURRENT METHOD TO LOW VOLATILITY COMPOUNDS AND PETROLEUM DISTILLATES
- APPLY TO SELECTED COATINGS CONSTITUENTS

DEVELOP AND EVALUATE PROCEDURES TO QUANTIFY REACTIVITIES AND UNCERTAINTIES FOR PETROLEUM DISTILLATES

**BECAUSE OF LIMITED FUNDING, NOT ALL INITIALLY PROPOSED WORK FOR REDUCING UNCERTAINTIES IN COATINGS VOCs COULD BE INCLUDED.**

# COMPONENTS OF PROPOSED EXTENSION TO CE-CERT/CARB COATINGS PROJECT

## CONDUCT ADDITIONAL ENVIRONMENTAL CHAMBER EXPERIMENTS USING NEW EPA FACILITY.

- SUFFICIENT FUNDING PROPOSED FOR ~40 EXPERIMENTS BASED ON CURRENT BUDGET ESTIMATES OF ~$4K PER RUN
- UP TO 6 COATINGS CONSTITUENTS CAN BE STUDIED AT ~7 RUNS PER CONSTITUENT
- CONSTITUENTS STUDIED WILL BE DETERMINED AFTER DISCUSSION WITH CARB AND RRAC.
- PROPOSAL INCLUDES ~12 RUNS WITH AEROSOL FORMATION POTENTIAL INFORMATION, COSTING ABOUT $400 ADDITIONAL PER RUN
- FACILITY CAN BE USED TO DETERMINE TEMPERATURE EFFECTS BUT THIS IS NOT INCLUDED IN CURRENT PROPOSAL.

## CONDUCT DIRECT REACTIVITY MEASUREMENTS ON MORE COMPLETE SET OF COATINGS CONSTITUENTS

- CURRENT FUNDING PROBABLY NOT SUFFICIENT FOR COMPLETE STUDY
- PROPOSED FUNDS SUFFICIENT FOR MINIMUM OF ~12 COMPOUNDS OR MIXTURES BASED ON CURRENT COSTS. COSTS MAY BE REDUCED.
- FUNDS FOR THIS TASK CAN BE USED FOR ADDITIONAL CHAMBER RUNS IF COSTS ARE REDUCED OR IF METHOD IS UNSUCCESSFUL.

# ENVIRONMENTAL CHAMBER STUDIES OF SELECTED COATINGS VOCs

## NEW LARGE ENVIRONMENTAL CHAMBER BEING DEVELOPED FOR THE EPA WILL BE EMPLOYED

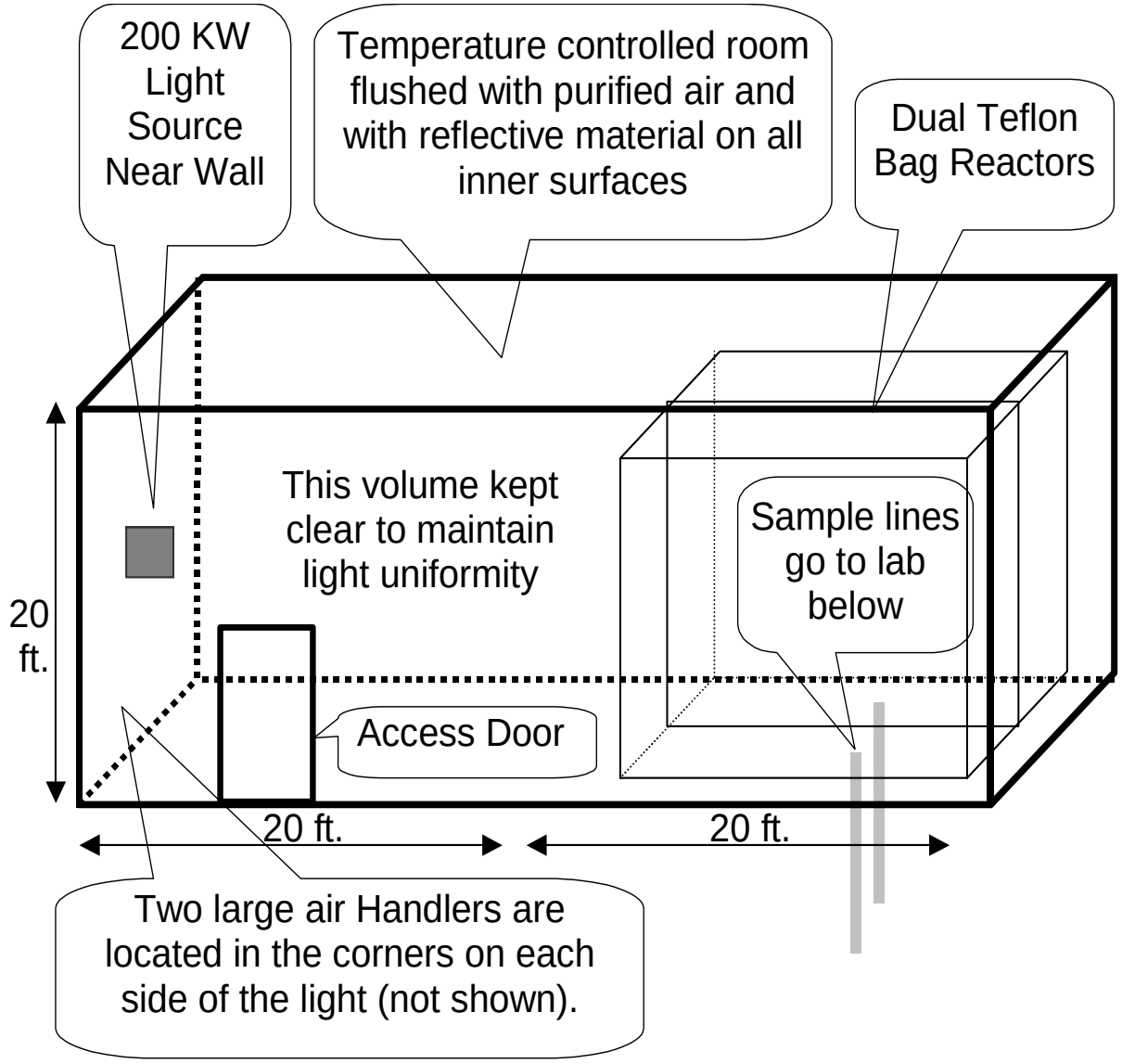
- CONSTRUCTED AND EVALUATED USING ~$3 MILLION FUNDING FROM THE U.S. EPA
- CAN OBTAIN DATA AT LOWER CONCENTRATIONS THAN PREVIOUSLY POSSIBLE
    - MORE REPRESENTATIVE OF CURRENT AMBIENT ATMOSPHERES
    - EASIER TO STUDY LOW VOLATILITY VOCs
- INSTRUMENTATION FOR MORE COMPREHENSIVE CHEMICAL ANALYSIS
- INSTRUMENTATION FOR INFORMATION ON AEROSOL (PM) IMPACTS

## METHODS FOR STUDIES OF LOW VOLATILITY VOCs BEING DEVELOPED FOR CURRENT PROJECT

## COMPOUNDS STUDIED TO BE SELECTED BASED ON REACTIVITY AND UNCERTAINTY PRIORITIZATION

- TEXANOL ALREADY BEING STUDIED
- REPRESENTATIVE PETROLEUM DISTILLATES NEXT PRIORITY
- ADDITIONAL WATER-BASED CONSTITUENTS MAY ALSO BE STUDIED

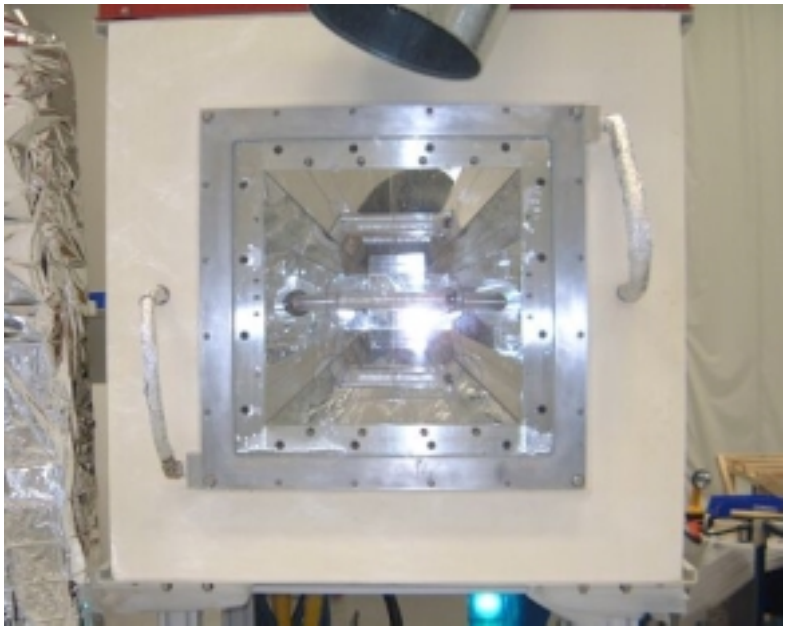
# DIAGRAM OF ENVIRONMENTAL CHAMBER AND TEMPERATURE-CONTROLLED ENCLOSURE

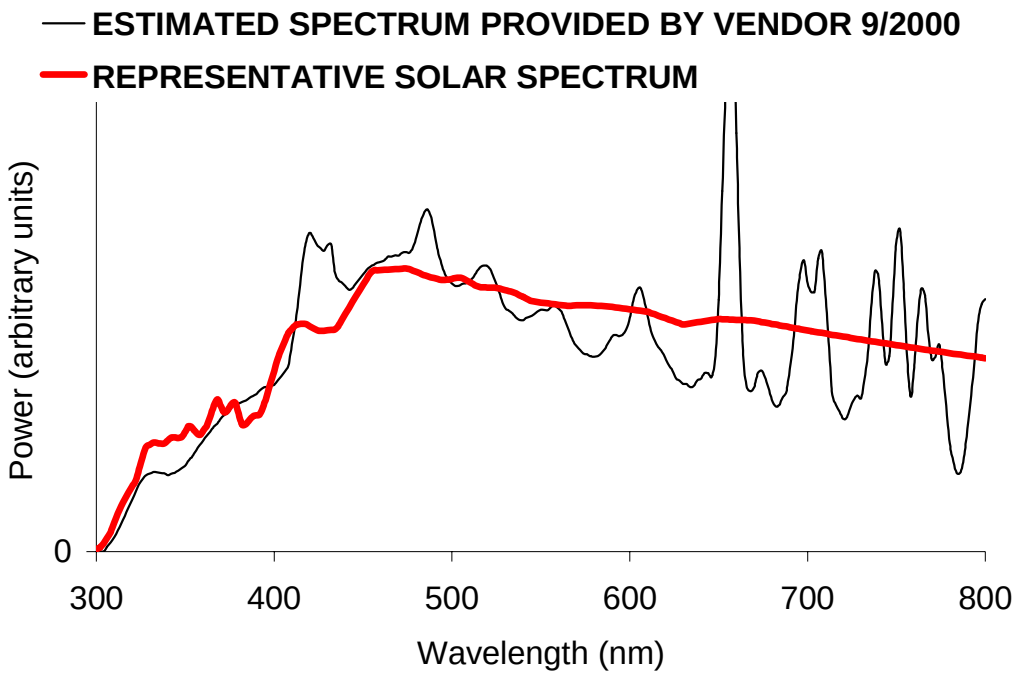


# CURRENT CHAMBER BUILDING AND LABORATORY

# CHAMBER ENCLOSURE AS OF 8/01

# LIGHT SOURCE (AT FACTORY) AND SPECTRUM SPECIFICATION





# PRELIMINARY RESULTS OF SURVEY OF COATINGS EMISSIONS REACTIVITY

## VOCs IN ARB COATINGS PROFILES ESTIMATED TO CONTRIBUTE MORE THAN 1% TO $O_3$

| MIR x EMIT | TYPE OF VOC | CHAM DATA? | MECH UNC'Y |
|---|---|---|---|
| | <u>WATER BASED COATINGS</u> | | |
| ~35% | Propylene Glycol | Yes | 1 |
| ~24% | Ethylene Glycol | No | 2 |
| ~11% | Texanol | No | 3 |
| ~6% | Butyl Carbitol | No | 3 |
| ~5% | Various Petroleum Distillates | Some | - |
| ~1% | Methyl Carbitol | No | 3 |
| ~1% | 2-Butoxyethanol | Yes | 1 |
| | <u>SOLVENT BASED COATINGS</u> | | |
| ~64% | Various Petroleum Distillates | Some | - |
| ~11% | Xylene Isomers | Yes | 2 |
| ~6% | Toluene | Yes | 2 |
| ~2% | 1,2,4-Trimethylbenzene | Yes | 2 |
| ~2% | Methyl Ethyl Ketone | Yes | 1 |
| ~2% | Ethanol | Yes | 1 |
| ~1% | 4-Methyl-2-Pentanone | Yes | 2 |

# VARIOUS TYPES OF PETROLEUM DISTILLATES IDENTIFIED IN PRELIMINARY CARB SURVEY

| COMMON NAME | BIN MIR | MIR x EMIT |
|---|---|---|
| Stoddard solvent | 2.5 | ~26% |
| Aromatic 100 | 7.5 | ~20% |
| Medium aliphatic solvent naphtha | 0.9 | ~15% |
| VM & painters naphtha | 2.0 | ~8% |
| Petroleum naphtha, heavy alkylate | 1.6 | ~6% |
| Distillate (petroleum), hydrotreated light | 1.4 | ~4% |
| Kerosene | 1.8 | ~2% |
| Petroleum ether | 1.6 | ~1% |
| Hydrotreated heavy naphtha | 1.2 | ~1% |
| Heavy aromatic naphtha solvent | 5.0 | ~1% |
| Solvent-refined heavy paraffinic distillate | 1.4 | ~0.5% |
| Naphtha | 2.1 | ~0.4% |
| Solvent naphtha, petroleum, heavy aliphatic | ~2 | ~0.1% |
| Heavy straight-run naphtha | ~2 | ~0.1% |

# DEVELOPMENT AND APPLICATION OF DIRECT REACTIVITY SCREENING METHOD

## DIRECT REACTIVITY

- RATE A VOC REACTS AND OXIDIZES NO, WHICH IS THE PROCESS THAT FORMS $O_3$
- ONE OF SEVERAL FACTORS AFFECTING REACTIVITY. THIS MAY BE MORE IMPORTANT IN THE ATMOSPHERE THAN IN CHAMBER STUDIES.
- GIVES MORE COMPLETE MECHANISM EVALUATION
- CAN TEST UNCERTAIN REACTIVITY ESTIMATES.
- CAN BE MEASURED AT LOWER COST THAN CONDUCTING CHAMBER EXPERIMENTS

## CURRENT STATUS

- METHOD BEING DEVELOPED AND EVALUATED FOR CARB CONTRACT THAT ENDS IN EARLY 2002
- ADDITIONAL WORK NEEDED BEFORE IT IS RELIABLE FOR LOW VOLATILITY COMPOUNDS AND PETROLEUM DISTILLATES
- CURRENT COATINGS CONTRACT COVERS COMPLETION OF EVALUATION AND INITIAL APPLICATION TO COATINGS VOCs
- ACTUAL AMOUNT OF ADDITIONAL RESOURCES NEEDED TO COMPLETE APPLICATION TO COATINGS VOCs IS NOT KNOW AT PRESENT TIME.

# MODEL PERFORMANCE IN SIMULATING DIRECT REACITIVITY RESULTS TO DATE